

# Metal-Free Cycloetherification by in Situ Generated *P*-Stereogenic $\alpha$ -Diazanium Intermediates: A Convergent Synthesis of Enantiomerically Pure Dihydrobenzooxaphospholes

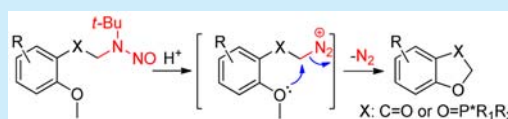
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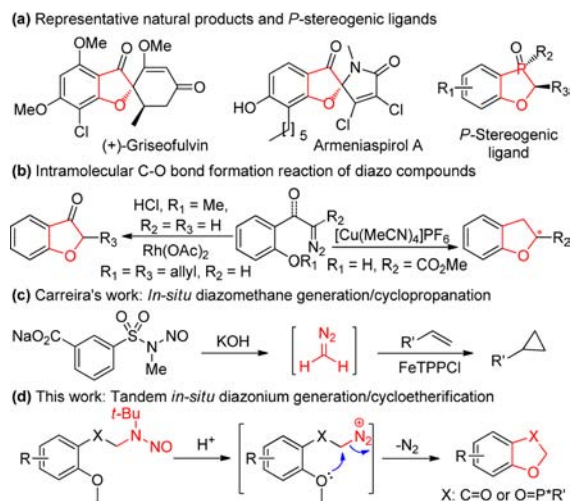
## Supporting Information

**ABSTRACT:** A metal-free tandem reaction, initiated by the generation of a diazonium cation and followed by cycloetherification, was developed. Acid-promoted de-*tert*-butylation of *N*-nitroso *N*-*tert*-butylamine was used to generate a diazonium cation in situ, demonstrating a new application of nitroso chemistry. This reaction was employed in the synthesis of substituted benzofuran-3(2*H*)-ones and dihydrobenzo[*d*][1,3]oxaphosphole 3-oxides.



Dihydrobenzofuran derivatives, such as benzofuran-3(2*H*)-ones, are important building blocks for a variety of natural products and pharmaceuticals (Scheme 1a).<sup>1</sup> Today, the

## Scheme 1. Examples of Synthesis of Diazo Intermediates and Applications



structurally related *P*-stereogenic chiral 2,3-dihydrobenzo[*d*]-[1,3]oxaphospholes and their corresponding 3-oxides are receiving significant attention due to their applications as chiral ligands in the rapidly evolving field of asymmetric catalysis.<sup>2</sup> Numerous methods have been reported for the construction of the tetrahydrofuran ring of dihydrobenzofurans and benzofuran-3(2*H*)-ones that describes the intramolecular C–O bond formation via a diazo intermediate.<sup>3</sup> The initial exploration of this reaction can be traced back to the conversion of  $\alpha$ -diazo-*o*-

methoxyacetophenone to coumaranone under a catalytic amount of hydrochloric acid<sup>4b</sup> and later to the conversion of 1-[2-(allyloxy)phenyl]-2-diazoethanone to 2-allylbenzofuran-3(2*H*)-one via a rhodium-catalyzed [2,3]-sigmatropic rearrangement of the oxonium ylides.<sup>4</sup> In 1991, Pirrung reported the asymmetric total synthesis of (+)-griseofulvin using a rhodium-catalyzed cyclization of a diazo intermediate to construct the benzofuran-3(2*H*)-one core.<sup>5</sup> Recently, Zhou and co-workers reported a copper-catalyzed enantioselective intramolecular insertion reaction of carbenoids into a phenolic O–H bond as a novel strategy for the synthesis of chiral 2-carboxydihydrobenzofurans (Scheme 1b).<sup>6</sup> However, the inherent acute toxicity and explosive nature of preformed diazo compounds raises significant concerns.<sup>7</sup> In this respect, methodologies involving in situ generation of diazo intermediates are preferable and of wide interest.<sup>8</sup> For example, Carreira and co-workers reported the in situ generation of diazomethane in a cyclopropanation cascade reaction using a water-soluble Diazald derivative (Scheme 1c).<sup>9</sup> Herein, we report a metal-free, tandem reaction involving acid-promoted de-*tert*-butylation of *N*-nitroso-*N*-*tert*-butylamine to generate a diazonium cation in situ, followed by cycloetherification to give substituted benzofuran-3(2*H*)-ones and *P*-stereogenic chiral dihydrobenzo[*d*][1,3]oxaphosphole 3-oxides without erosion of chirality at the phosphorus center (Scheme 1d).

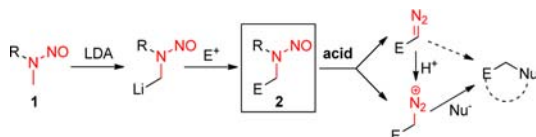
Diazomethane can be generated from *N*-nitroso precursors under basic conditions; examples include Diazald,<sup>9,10</sup> nitrosomethylurea,<sup>11</sup> and *N*-nitroso- $\beta$ -methylaminoisobutyl methyl ketone.<sup>12</sup> Mindful of these methodologies, we set out to design an alkaline stable, *N*-nitroso reagent that could generate the

Received: January 6, 2017

Published: February 3, 2017

metalated nitrosoamine and, subsequently, capture an electrophile to generate the key intermediate **2** (Scheme 2). Acidification of **2** could deprotect the *N*-nitrosoamine to furnish the substituted diazo intermediate in situ, which could then react with a nucleophile.

Scheme 2. Strategy for the Synthesis of Diazo Intermediates



To test our strategy, the acid-promoted conversion of **2** to **3** was surveyed under various conditions (Table 1). As anticipated,

Table 1. Survey of Reaction Conditions for Diazonium-Mediated Cycloetheration in the Synthesis of Benzofuran-3(2*H*)-ones<sup>a</sup>

| entry | 2  | acid | solvent     | time (h) | yield <sup>b</sup> (%) |
|-------|----|------|-------------|----------|------------------------|
| 1     | 2a | HCl  | DCM         | 24       | 0                      |
| 2     | 2b | HCl  | DCM         | 24       | 0                      |
| 3     | 2a | TFA  | DCM         | 24       | 0                      |
| 4     | 2b | TFA  | DCM         | 24       | 0                      |
| 5     | 2a | TfOH | DCM         | 5        | 0                      |
| 6     | 2b | TfOH | DCM         | 12       | 71 (67)                |
| 7     | 2b | TfOH | toluene     | 8        | 68 (60)                |
| 8     | 2b | TfOH | benzene     | 8        | 66                     |
| 9     | 2b | TfOH | cyclohexane | 8        | 23                     |

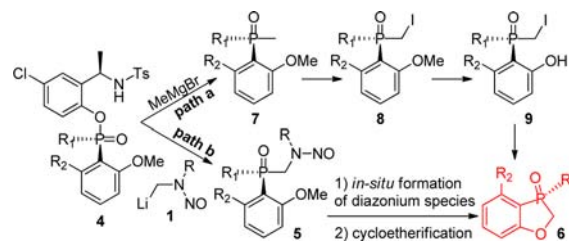
<sup>a</sup>All reactions were carried out with **2** (0.10 mmol) and acid (0.5 mmol) in solvent (1 mL) at room temperature. <sup>b</sup>NMR-based estimated yields using CH<sub>2</sub>Br<sub>2</sub> as an internal standard, isolated yields in parentheses.

significant reactivity differences were observed between the acid-labile *tert*-butyl analogue **2b** and the methyl-substituted analogue **2a** (entry 5 vs 6; only decomposition products were observed in entry 5). We did not observe any products formed with **2a**, irrespective of the reaction conditions. When **2b** was used, the desired product was obtained, but the reaction rate and yield were highly dependent on the acid strength and the solvent (e.g., entry 4 vs 6). Better results were obtained when TfOH was used as the acid in a nonpolar solvent, such as DCM, benzene, or toluene, from which an isolated yield of 60–70% was obtained over two steps. Encouraged by these results, we turned our attention to the synthesis of the *P*-stereogenic derivatives of **6**.

Previously, Han and co-workers reported the synthesis of **6** (Scheme 3, path a). Reaction of chiral phosphinates **4** with either MeMgX or MeLi afforded the phosphine oxide **7** in high yield and enantioselectivity.<sup>2b,c</sup> Iodination of the *P*-methyl followed by demethylation of **8** provided the phenol **9**, which upon treatment with base afforded the *P*-chiral 2,3-dihydrobenzo[*d*][1,3]-oxaphosphole 3-oxide **6**.<sup>2a</sup> We presumed that the synthesis of **6** would be more straightforward if the *P*-chiral *N*-nitroso- $\alpha$ -aminophosphine oxide **5** was used as an intermediate (Scheme 3; path b).

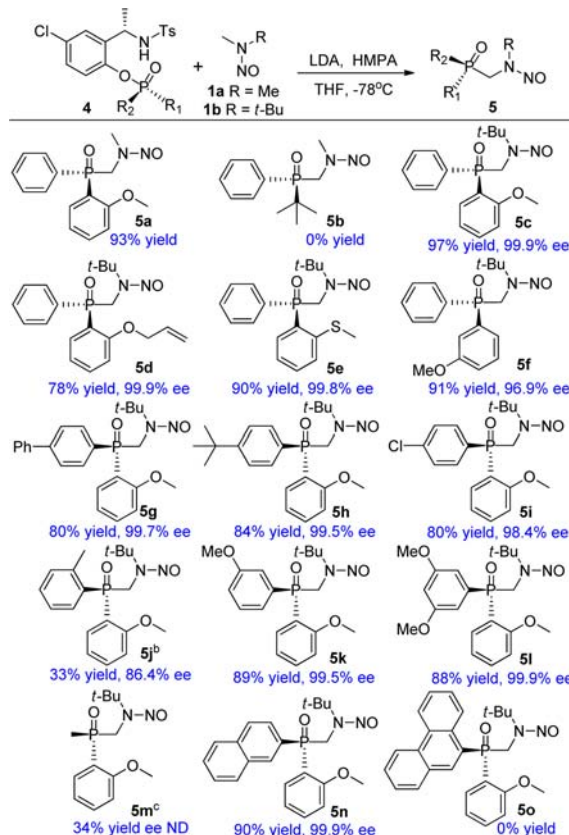
The synthesis of **5** was investigated via the reaction of **4** with metalated nitrosoamine **1** (Scheme 3; path b). After extensive

Scheme 3. Synthesis of *P*-Stereogenic Chiral Dihydrobenzoxaphospholes via in Situ Generated Diazo Intermediates



optimization of the reaction conditions,<sup>13</sup> we found that this reaction proceeded most efficiently when **4** was treated with 6 equiv of *N*-nitrosoamine **1** and 4 equiv of LDA in the presence of HMPA at  $-78^{\circ}\text{C}$ , affording **5** in high to excellent yield and enantiomeric purity (Scheme 4). Not surprisingly, the outcome

Scheme 4. Synthesis of *P*-Stereogenic *N*-Nitroso- $\alpha$ -Aminophosphine Oxides **5**<sup>a</sup>



<sup>a</sup>All reactions were carried out with **4** (1 equiv), nitrosoamine **1** (6 equiv), LDA (4 equiv), and HMPA (10 equiv) in THF at  $-78^{\circ}\text{C}$  unless otherwise noted (isolated yield). Stereochemistry and % ee determined by chiral HPLC.<sup>13</sup> <sup>b</sup>Temperature at  $-41^{\circ}\text{C}$ . <sup>c</sup>Nitrosoamine **3** (8 equiv).

of this substitution reaction was modulated by the steric hindrance around the phosphorus atom. For example, analogues having a *tert*-butyl or phenanthrene substituent on the phosphorus did not give any appreciable amount of the desired products **5b** and **5o**, respectively, even after prolonged reaction time and/or higher temperatures. Similarly, product **5j**, having two *ortho*-substituent phenyls on the phosphorus was obtained in

only 33% yield and a relatively lower enantiomeric purity. Compound **5m** was also obtained in lower yield (34%), likely due to the activated methyl on the phosphorus, which is unstable under the strongly basic conditions. It is noteworthy that the use of *N*-nitrosodimethylamine **1a** gave **5** as a mixture of two rotamers (1:1 mixture, presumably due to the high energy barrier of the N–NO rotation or N–O inversion),<sup>14</sup> whereas, the products derived from **1b** consisted of only one rotamer, likely due to the steric bulk of the *tert*-butyl group. It is important to note that reagent **1b** and the *P*-chiral *N*-nitroso- $\alpha$ -amino-phosphine oxide **5c** were thermally stable up to 230 °C;<sup>13</sup> the latter compound may represent a unique precursor of yet undeveloped *P*-chiral *P,N*-nitroso bidentate ligands.<sup>15</sup>

We subsequently focused on the synthesis of **6a** to evaluate our strategy and optimize the conditions for the tandem diazonium generation and cycloetherification reaction (Table 2). Treatment

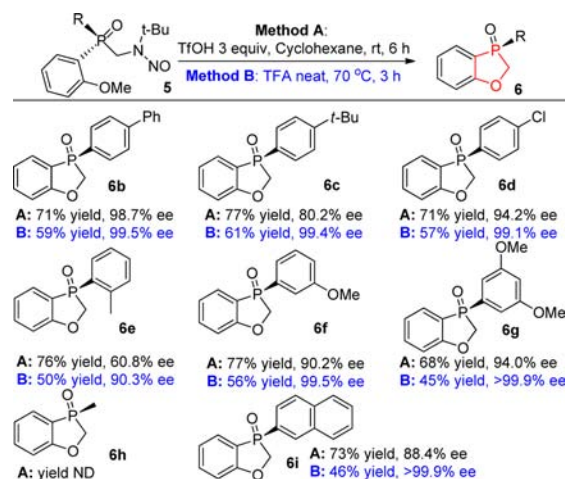
Table 2. Optimization for Cycloetherification Reaction

| entry | solvent                       | acid | temp (°C) | time (h) | yield <sup>a</sup> (%) |
|-------|-------------------------------|------|-----------|----------|------------------------|
| 1     | DCM                           | TfOH | rt        | 4        | 65                     |
| 2     | toluene                       | TfOH | rt        | 4        | 60                     |
| 3     | CH <sub>3</sub> CN            | TfOH | rt        | 4        | 27                     |
| 4     | THF                           | TfOH | rt        | 4        | 37                     |
| 5     | PhCl                          | TfOH | rt        | 4        | 71                     |
| 6     | ODCB                          | TfOH | rt        | 4        | 69                     |
| 7     | C <sub>6</sub> F <sub>6</sub> | TfOH | rt        | 4        | 69                     |
| 8     | hexane                        | TfOH | rt        | 6        | 77                     |
| 9     | cyclohexane                   | TfOH | rt        | 6        | 81 (74)                |
| 10    |                               | TFA  | 70        | 3        | 63 (60)                |

<sup>a</sup>Estimated yield based on <sup>31</sup>P NMR; isolated yield in parentheses.

of **5c** with 3 equiv of TfOH in DCM gave compound **6a** in 65% yield (based on <sup>31</sup>P NMR) after 4 h at room temperature (Table 2, entry 1). Other nonpolar solvents (entries 2, 5, 6, and 7) gave fairly similar yields (60–70%). However, polar solvents gave significantly lower yields (entries 3 and 4). A longer reaction time with highly nonpolar solvents, such as hexane and cyclohexane, gave slightly better yields (entries 8 and 9). Interestingly, under the latter conditions, both the starting material and the product were mostly insoluble, and vigorous stirring of the reaction mixture had to be maintained. It is reasonable to assume that decreasing the polarity of the solvent, as well as the corresponding dielectric constant, decreases the extent of solvation of the polar transition state (diazonium cation), leading to fewer side reactions, without any adverse effects on the efficiency of the intramolecular cycloetherification.<sup>16</sup> The use of different acids also affected the enantiomeric purity of **6a**. For example, a 97.2:2.8 er was observed with TfOH (Table 2, entry 9), whereas >99.9:0.1 er and 60% isolated yield were observed when neat TFA was used at 70 °C for 3 h (entry 10). Under two optimized sets of conditions (Table 2, entries 9 and 10), a number of other structurally diverse *P*-stereogenic dihydrobenzooxaphosphole 3-oxides **6** were prepared in good yield and high enantiomeric purity as shown in Scheme 5. Although all reactions proceeded efficiently, use of neat TFA at 70 °C for 3 h provided **6** in high enantiomeric integrity, but in slightly diminished yield (method B). Whereas, in some cases the use of TfOH in

Scheme 5. Synthesis of Substituted *P*-Stereogenic 2,3-Dihydrobenzo[*d*][1,3]oxaphosphole 3-Oxides **6**<sup>a</sup>

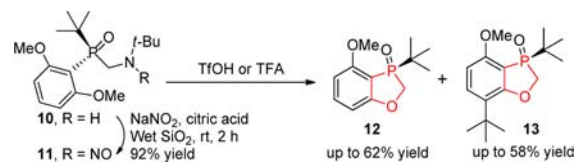


<sup>a</sup>Isolated yield; % ee was determined by chiral HPLC.

cyclohexane at room temperature afforded **6** with lower enantiomeric purity (method A).

The *P*-chiral dihydrobenzooxaphosphole 3-oxide **12** was also prepared using the same methodology (Scheme 6). It is

Scheme 6. Synthesis of *P*-Chiral 3-*tert*-Butyl-2,3-dihydrobenzo[*d*][1,3]-oxaphospholes



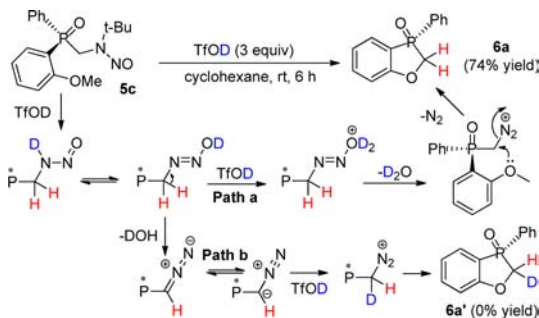
noteworthy that compound **12** is the precursor of many efficient *P*-stereogenic chiral phosphine ligands, such as BIBOPs,<sup>17a</sup> BI-DIME,<sup>17b,c</sup> JoshPhos,<sup>17</sup> AntPhos,<sup>17e</sup> LalithPhos,<sup>17f</sup> BoQPhos,<sup>17f</sup> and POP.<sup>17g</sup> The precursor compound **11** was synthesized via nitrosation of **10**, which was previously prepared by *tert*-butylation of the corresponding iodide intermediate. Treatment of **11** with various acidic conditions<sup>13</sup> gave the desired product **12** in addition to the side product **13**, likely due to a competing Friedel–Crafts alkylation reaction between the electron-rich aromatic ring and *tert*-butyl cation eliminated during deprotection of compound **11**. Treatment of **11** with 5 equiv of TfOH in cyclohexane favored the formation of the side product **13** (58% isolated yield, 91.6% ee), whereas changing the solvent to DCM gave predominantly the desired product **12** in 62% isolated yield and 99:1 er.

Intrigued by the Friedel–Crafts side reaction, we decided to probe the mechanism of the cycloetheration step (Scheme 7). In the presence of TfOD, compound **6a** was formed without any observable amount of the  $\alpha$ -deuterated analogue **6a'**, suggesting that the  $\alpha$ -diazonium cation was generated directly via “path a” without proton exchange at the C- $\alpha$  position (path b). Additionally, a model reaction with substrate **5f**, lacking the nucleophilic *o*-methoxy group, led mainly to the formation of compounds **14** (40% yield), **15**, and **16** (Scheme 8).

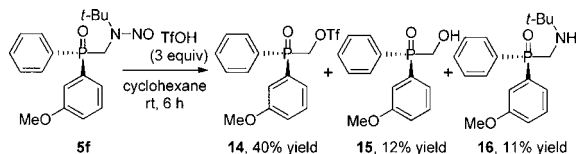
In summary, we developed an effective acid-promoted, metal-free tandem reaction for the in situ generation of a diazonium cation and subsequent cycloetherification to give a series of substituted benzofuran-3(2*H*)-ones and enantiopure *P*-stereo-



## Scheme 7. Mechanistic Investigations



## Scheme 8. Control Experiment



genic chiral 2,3-dihydrobenzo[*d*][1,3]oxaphosphole 3-oxides. The acid-promoted de-*tert*-butylation of *N*-nitroso-*N*-*tert*-butylamine generates a very active diazonium cation in situ, demonstrating an innovative application of classical nitroso chemistry. The in situ generation of a diazonium cation can be considered equivalent to a carbocation and, consequently, may be useful in other synthetic applications such as the Tiffeneau–Demjanov ring-expansion reaction. The *N*-nitroso- $\alpha$ -amino-phosphine oxides 5 represent unique reagents that can be readily transformed to *P*-stereogenic chiral  $\alpha$ -aminophosphine oxides.

## ■ ASSOCIATED CONTENT

## S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b00051.

Experimental procedures and characterization details (PDF)

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## Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

We are grateful for financial support from the Natural Sciences and Engineering Research Council of Canada (NSERC) and Boehringer-Ingelheim Pharmaceuticals, Inc.

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